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EPR Studies of Divalent Vanadium Ions in $CdBr_2$ and $CdCl_2$

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The electron paramagnetic resonance (EPR) spectra of a V^{2+} center in $CdBr_2$ and $CdCl_2$ single crystals were investigated at LNT. The angular dependence of fine structures in the spectra shows that the V^{2+} centers have D_{3d} symmetry and that V^{2+} ions are supposed to replace Cd^{2+} ions of the host crystals. The observed angular dependence was analyzed in terms of a spin Hamiltonian of axial symmetry. The best fitted values of parameters with experiments are $g_{//}=1.972$, $g_{\perp}=1.968$ and $|D|=0.213$ cm^{-1} for $CdCl_2:V^{2+}$ and $g_{//}=1.981$, $g_{\perp}=1.973$ and $|D|=0.155$ cm^{-1} for $CdBr_2:V^{2+}$. Each fine structures are accompanied by eight sharp lines of the hyperfine structures due to the vanadium nuclear spin ($I=7/2$). The values of the elements of the hyperfine coupling tensor were obtained as $A_{//}=80.2\times10^{-4}$ cm^{-1} and $A_{\perp}=94.1\times10^{-4}$ cm^{-1} for $CdCl_2:V^{2+}$ and $A_{//}=88.2\times10^{-4}$ cm^{-1} and $A_{\perp}=70.7\times10^{-4}$ cm^{-1} for $CdBr_2:V^{2+}$.

1. Introduction

Paramagnetic resonance absorption of V^{2+} ion has been investigated by many workers for the various host crystals.[1)-11)]

The V^{2+} ion has $3d^3$ electronic configuration as Cr^{3+} ion. The ground state of the free ion, according to the Hund's rule, is ^4F which has the four-fold orbital degeneracy. Group theoretical arguments tell us the the ^4F level will split into an orbital singlet $^4A_{2g}$, an orbital triplet $^4T_{2g}$ and an orbital triplet $^4T_{1g}$ in an octahedral crystal field. The ground state is the $^4A_{2g}$ state which is lower than the other two states. In the trigonal crystal field, the $^4A_{2g}$ state will remain as itself, but the spin-orbit coupling will remove spin degeneracies, splitting the quadruplet

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into two Kramers doublets, i.e. $E_{1/2}(\Gamma_4)$ and $E_{3/2}(\Gamma_5+\Gamma_6)$.

The $CdCl_2$,$CdBr_2$ crystals are typical layer ionic crystals which belong to $CdCl_2$ type structure. The symmetry was determined by Pauling and Hoard[12] and rhombohedral, space group D^5_{3d}, with one $CdCl_2$ per unit cell. The Cd^{2+} ions are located on the center of the MX_6 type octahedral complex which consists of six surrounding nearest neighbor halogen ions. This octahedral complex is a little compressed along the c-axis, and have the D_{3d}symmetry.

The V^{2+}ions presumably occur substitutionally for Cd^{2+} ions as an impurity.

In this paper, will be presented the results of an investigation on the EPR of V^{2+}ion in $CdCl_2$ and $CdBr_2$ single crystals. The experimental results will be analyzed by using a spin Hamiltonian of D_{3d} symmetry.

2. Experimentals

Measurements were performed on $CdBr_2$ and $CdCl_2$ crystals doped with VCl_3. The single crystals were grown from the melt by Bridgman method in quartz ampoules. During the processes of crystal growth, a large part of trivalent vanadium ions are converted into divalent ones, which is confirmed by the present experimental results.

The specimens were cut from the single crystals into the size of about $2 \times 2 \times 10$ mm^3, and were sealed into evacuated quartz capillaries of inner diameter of about 4.0 mm.

The EPR measurements were made with X-band EPR spectrometer at 77K (LNT). The direction of the static magnetic field is rotated in the plane containing the crystal c-axis, the three-fold axis , and the axis joining the V^{2+} ions, which is assumed to be at the Cd^{2+}ion site, to the neighboring halogen ion. In practice, the sample crystals were rotated around the two-fold axis of the crystal, which will be refferd as the v-axis later, and the direction of the static magnetic field was fixed. The intensity of the static magnetic field was measured by a proton meter.

3. Experimental Results

Fig.1 shows EPR spectra of the $CdBr_2:V^{2+}$ crystal at 77K. The spectrum in the upper part of the figure was obtained with static magnetic field parallel to the crystal c-axis , $\theta=0°$ ($H/\!/c$) , and that in the lower part shows one obtained at $\theta=90°$ ($H\perp c$). It can be seen in the figure that fine the structures spread from 100 Oe up to 6500 Oe. Each fine structure spilits into eight sharp lines. This spiliting is due to the hyperfine interaction of an unpaired electron spin with the vanadium nuclear spin ($I=7/2$). From the intensity of the $\theta=0°$ spectrum, it can be found that the structures at about 500 Oe, 3500 Oe and 6000 Oe are attributed to the allowed transition, and those at about 1200 Oe and 4000 Oe are attributed to the forbidden transition. In the $\theta=90°$ spectrum, structures at about 2300 Oe, 3000 Oe and 5000 Oe correspond to the allowed transition, and the one at 1600 Oe correspond to the forbidden transition. In this spectrum, eight lines due to the hyperfine interaction are clearly resolved.

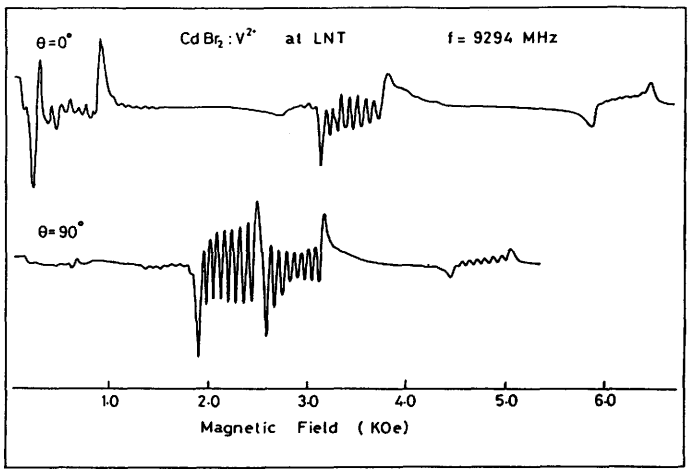

Fig. 1 EPR spectra of the V^{2+} center in $CdBr_2$ crystal at 77 K. The spectrum in the upper is for the case of $\theta=0°$ and in the lower part for $\theta=90°$, where is the angle between the c-axis and the direction of the static magnetic field. Each fine structure splits into eight sharp lines, which is due to the hyperfine interaction of an unpaired electron spin with the vanadium nuclear spin.

The spectra shown in Fig. 2 were obtained with the $CdCl_2:V^{2+}$ crystal at 77 K. The upper and the lower spectra were obtained for the case of $\theta=0^\circ$ ($H/\!/c$), and $\theta=90^\circ$ ($H\perp c$) respectively. The eight sharp lines of hyperfine structures appear clearly in the $\theta=90^\circ$ spectrum. It is assigned from their intensity that the structures of the $\theta=0^\circ$ spectrum at about the 1100 Oe and 3500 Oe are due to the allowed transition and those at about 700 Oe and 4000 Oe due to the forbidden one. In the $\theta=90^\circ$ spectrum, the structure at about 2000 Oe may be assigned to the allowed transition and that around 5500 Oe, which was detected with the higher sensitivity, due to the forbidden transition.

In the $CdCl_2:V^{2+}$ crystals, other several weak structures can be observed with the increased sensitivity of the detector. Results obtained for $\theta=90^\circ$ are shown in Fig. 3. The structures are discerned around 1000 Oe, 3000 Oe and 6500 Oe. The structure in the region from 2500 Oe to 4500 Oe consists of many sharp lines, the spacing of which is about a half of that between the hyperfine structures. These many line structures are supposed to be caused by the superposition of superhyperfine structures, due to the interaction of the electron spin with the ligand chlorine nuclear spin, on the hyperfine structures due to the interaction of the electron spin with vanadium nuclear spin. The structure at about 1000 Oe is very broad, and eight hyperfine structures are supposed to overlap with each other.

The angular dependence of the spectra of the $CdBr_2:V^{2+}$ crystal at LNT is shown in Fig. 4 (a). The points denote the positions of each fine structure, that is, the central positions of the observed eight hyperfine structures. Solid lines represent angular variation of the spectral positions caliculated by using appropriate values of parameters described later. This angular dependence points out that the V^{2+} center is subjected to strong influence of the crystal field of three-fold symmetry, and that Cd^{2+} ion is replaced by the V^{2+} ion and the local symmetry around the V^{2+} center is D_{3d}.

Fig. 4 (b) shows the angular dependence of the fine structures of $CdCl_2:V^{2+}$ crystal at LNT. In this figure, the points and solid curves are the same as described above for $CdBr_2:V^{2+}$. As in the case of $CdBr_2:V^{2+}$, it would be apparent from this angular dependence the V^{2+} centers in $CdCl_2$ have a local symmetry of D_{3d}.

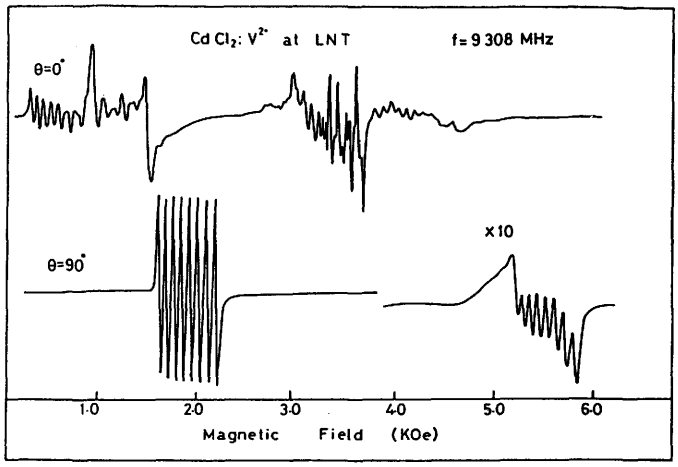

Fig. 2 The EPR spectra of the V^{2+} center in $CdCl_2$ at LNT. The spectra in the upper and the lower were obtained for the case of $\Theta=0^{\circ}$ and $\Theta=90^{\circ}$ respectively. The eight sharp lines of hyperfine structures appear clealy in the spectra.

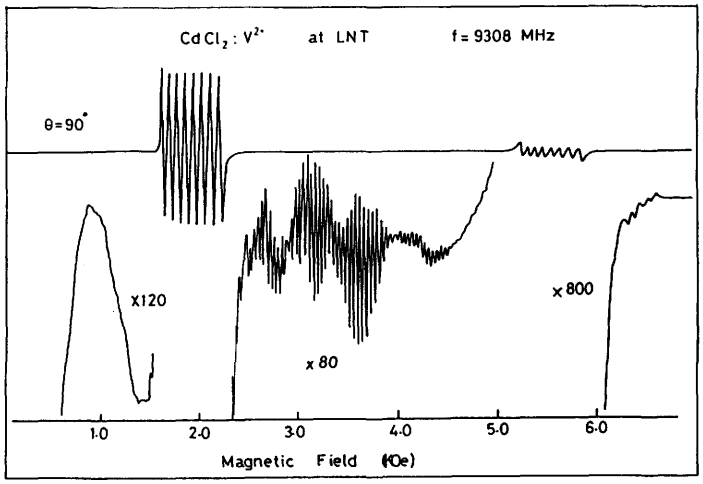

Fig. 3 The EPR spectra of V^{2+} center in $CdCl_2$ with the static magnetic field papendicular to the c-axis. Increasing the sensitivity of the detector, other several week structures can be observed. The structure in the region from 2500 Oe to 4500 Oe consists of many sharp lines. These are supposed to be caused by superposition of superhyperfine structures on the hyperfine structures.

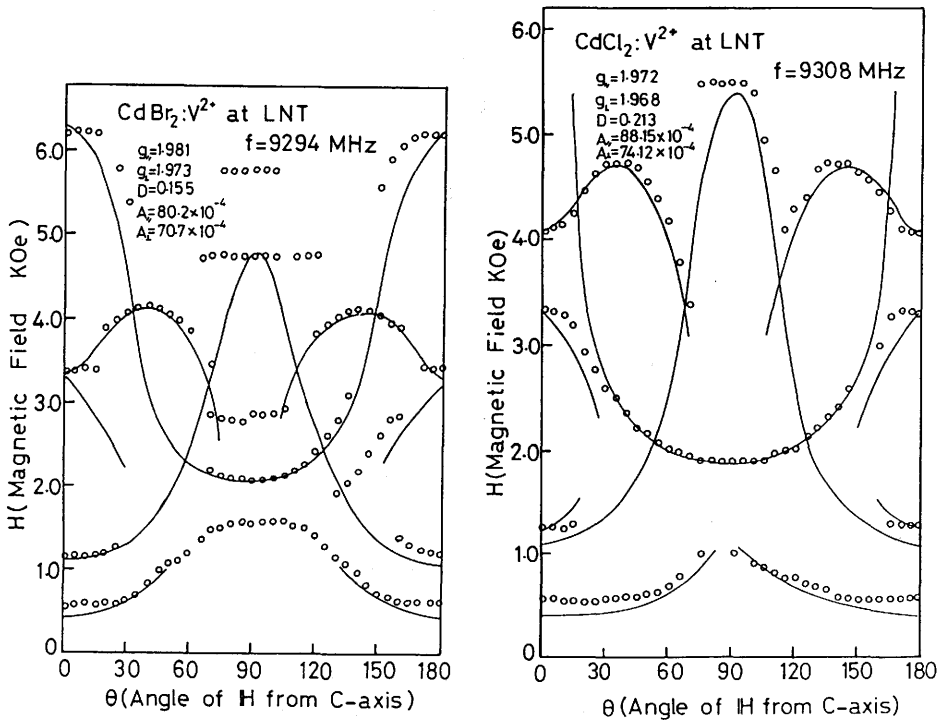

Fig. 4 The angular dependence of EPR spectrum of the V^{2+} center measured at LNT.
(a): $CdBr_2:V^{2+}$ (b): $CdCl_2:V^{2+}$

4. Analysis and Discussion

It is supposed from the experimental results on the angular dependence that the V^{2+} ion is located at the center of an octahedron composed of six nearest neighbor halogen ions as shown in Fig. 5. This octahedron is not regular but comoressed along the crystal c-axis. Thus the symmetry of this center is D_{3d} with one three-fold axis and three two-fold axes.

It is convenient for the description of the experimental results to introduce two rectangular coordinate system, which are illustrated in the figure as the (u,v,w) system and the (x,y,z) system. The origin of figure as the (u,v,w) system is located at the center of the octahedron and the w-axis is taken parallel to the c-axis. The v-axis is in the direction of one of the two-fold axis in the plane of the cadmium ion layer.

The u-axis is taken to be perpendicular to both the v- and w-axis.

The (x,y,z) system is obtained by rotating the (u,v,w) system with the Eulerian angle $\alpha = 0^{\circ}$, $\beta = -\cos^{-1}\sqrt{1/3}$ and $\gamma = -45^{\circ}$. In this rectangular coordinate system, the u-, v- and w-axis are located in the directions of $[11\bar{2}]$, $[\bar{1}10]$ and [111], respectively. Strictly speaking, the directions joining the V^{2+} ion to the neighboring Cl^{-} ions deviate a little from these of the x-, y- and z-axis. However, it may be said the nearest neighbor ions lie on the x-, y- or z-axis when there is no confusion.

In the EPR experiments, the static magnetic field was rotated around the v-axis, i.e. in the u-w plane as is mentioned.

It is noted that the z-axis lies in this u-w plane. The direction of the sttic magnetic field, therefore, is expressed in the (u,v,w) system by the variable zenith angle.

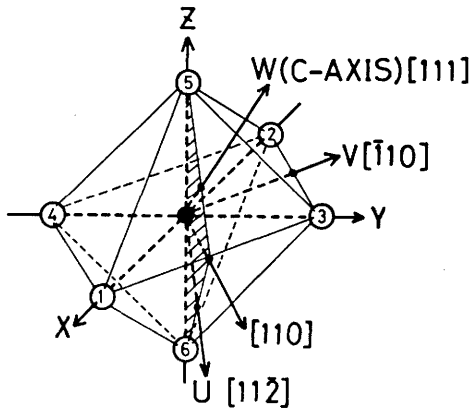

Fig. 1 The model of the V^{2+} center and the coordinate systems (u,v,w) and (x,y,z). The black and the white circles represent the V^{2+} ion and the halogen ions respectively. The w-axis is parallel to the c-axis. The v-axis is in the direction of one of the two-fold axes in the plane of the cadmium ion layer. The u-axis is taken to be perpendicular to both the w- and v-axis. The (x,y,z) system is obtained by rotating the (u,v,w) system. With reference to the (x,y,z) system, the u-, v- and w-axis are located in the directions of $[11\bar{2}]$, $[\bar{1}10]$ and [111]. Strictly speaking, the x-, y- and z-axis do not pass through the center of the Cl^{-} ion.

From the angular dependence of the spectral positions as shown in Fig. 4 (a) and (b), the axial field parallel to the c-axis is fairly strong and can not be neglected in treating the spectrum of V^{2+} cnters. Thus, the spin Hamiltonian, which will be used to analyze the angular dependence of the spectra, is required to have three-fold axial symmetry, that is, the tensors g, D and A in the spin Hamiltonian should be invariant under the symmetry operations of D_{3d} point group. The tensors g, D and A for the V^{2+} center are written in the (u,v,w) system as:

$$g(u,v,w)=\begin{pmatrix} g_{\perp} & 0 & 0 \\ 0 & g_{\perp} & 0 \\ 0 & 0 & g_{\parallel} \end{pmatrix} \qquad (1)$$

$$D(u,v,w)=\begin{pmatrix} D_{\perp} & 0 & 0 \\ 0 & D_{\perp} & 0 \\ 0 & 0 & D_{\parallel} \end{pmatrix} \qquad (2)$$

$$A(u,v,w)=\begin{pmatrix} A_{\perp} & 0 & 0 \\ 0 & A_{\perp} & 0 \\ 0 & 0 & A_{\parallel} \end{pmatrix} \qquad (3)$$

where

$$\begin{aligned} g_{\perp} &= g_{uu} = g_{vv} = g_{xx} - g_{yy} \\ g_{\parallel} &= g_{ww} = g_{xx} + g_{yy} \end{aligned} \qquad (4)$$

$$\begin{aligned} D_{\perp} &= D_{uu} = D_{vv} = D_{xx} - D_{yy} \\ D_{\parallel} &= D_{ww} = D_{xx} + D_{yy} \end{aligned} \qquad (5)$$

$$\begin{aligned} A_{\perp} &= A_{uu} = A_{vv} = A_{xx} - A_{yy} \\ A_{\parallel} &= A_{ww} = A_{xx} + A_{yy} \end{aligned} \qquad (6)$$

In terms of the elements of these tensors, the spin Hamiltonian is written as follows:

$$\begin{aligned} \mathcal{H} &= g\beta \boldsymbol{HS} + \boldsymbol{SDS} + \boldsymbol{SAI} \\ &= \beta H(g_{\parallel}\cos\Theta . S_w + g_{\perp}\sin\Theta . S_u) + D(S_w^2 - S(S+1)/3) \\ &\quad + A_{\parallel} S_w I_w + A_{\perp}(S_u I_u + S_v I_v) \end{aligned} \qquad -----(7)$$

where β is Bohr magneton, H is the intensity of the static magnetic field, S is the electron spin operater and $I(=7/2)$ is the vanadium nuclear spin.

To analyze the angular dependence of fine structures given in Fig. 4 (a) and (b), the terms of the hyperfine interactions are also neglected.

The best fitted values of parameters $g_{\parallel}$, $g_{\perp}$ and D with experiments are shown in Table 1. The values of $A_{\parallel}$ and $A_{\perp}$ were obtained from the separation of the hyperfine structures in the $\Theta = 0^{\circ}$ and the $\Theta = 90^{\circ}$ spectra, respectively and they are also given in the table.

T = 77 K	$g_{\parallel}$	$g_{\perp}$	$\lvert D \rvert$ (cm^{-1})	A (10^{-4} cm^{-1})	A (10^{-4} cm^{-1})
$CdCl_2:V^{2+}$	1.972	1.968	0.213	80.2	94.1
$CdBr_2:V^{2+}$	1.981	1.973	0.155	88.1	70.7
$CdI_2:V^{2+}$	2.01	2.01	0.099	-64.0	-64.0

Table 1 The best fitted values of parameters for the V^{2+} centers in $CdCl_2$, $CdBr_2$, CdI_2 .

In this table the values of parameters for $CdI_2:V^{2+}$ [10] are listed to compare with those in the present system of $CdCl_2:V^{2+}$ and $CdBr_2:V^{2+}$. The angular dependence calculated by using these values of each parameter are shown with solid curves in Fig. 4 (a) and (b). The agreement between measured and calculated values are fairly good.

Effective g-value sift from the value of free electron is caused mainly by mixing the $^4T_{2g}$ excited state to the $^4A_{2g}$ ground state by spin-orbit coupling in the O_h crystal field. In the present cases, the g-values are close to that of a free electron spin. This is reasonable because the crystal field splitting energy, 10Dq, between the ground $^4A_{2g}$ state and the excited $^4T_{2g}$ state of the V^{2+} center are much larger than the spin-orbit interaction. The spin-orbit mixing gives a contribution to the g-value

$$\Delta g = g - 2.0023 = -\frac{8}{3}\frac{\kappa'\zeta'}{10Dq} \qquad (8)$$

where κ' is the reduction factor for the orbital momentum and ζ' is the spin-orbit coupling constant between e_g and t_{2g} orbital.

In Table 2 are shown the results of the reduceed spin-orbit coupling constant calculated for the V^{2+} centers in cadmium halide crystals, by using the average g-value, i.e. $g_{av} = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$ and the 10Dq values of the corresponding pure vanadium dihalides.

host	g_{av}	10Dq (cm^{-1})	$\kappa'\zeta'$(cm^{-1})
$CdCl_2$	1.969	9200 [11]	115
$CdBr_2$	1.976	8500	83.8
CdI_2	2.01	7870 [10]	-23.0

Table 2 The reduced spin-orbit coupling constant calculated for the V^{2+} centers in cadmium halide crystals.

The value of 10Dq for the $CdBr_2:V^{2+}$ crystal is inferred from the values for VCl_2 and VI_2 by taking the "Spectro chemical series" into account. The value of $\kappa'\zeta'$ obtained in this way are very different from the spin-orbit coupling constant $\zeta = 167\ cm^{-1}$[13] of the free V^{2+} ion. This is caused mainly by the contribution from the spin-orbit coupling with the ligands. From the fact that the value of κ' decrease in order of $CdCl_2$, $CdBr_2$ and CdI_2 crystals, the degree of covalency increases in this order.

5. Conclusion

The V^{2+} ions in $CdCl_2$ and $CdBr_2$ crystals were found to replace the Cd^{2+} ions of the host lattice with them and to compose the MX_6 type octahedral complex which consists of the central V^{2+} ion and six neighboring halogen ions. The angular dependence of the fine structures in the EPR spectra can be fitted by using a g-tensor and a D-tensor of D_{3d} symmetry. Each fine structure is accompanied with eight hyperfine structures due to the vanadium nuclear spin $I=7/2$. In $CdCl_2:V^{2+}$ were also observed superhyperfine structures due to the interaction between the electron spin and the nuclear spin of the ligand halogen ions. The reduction factors for the orbital momentum, which is caused by the mixing between the ground $^4A_{2g}$ state and the excited $^4T_{2g}$ state by spin-orbit coupling, were estimated for the V^{2+} centers in cadmium halide crystals and it was concluded that the degree of covalency increases in order of $CdCl_2$, $CdBr_2$ and CdI_2 crystals.

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